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Local Relaxation around Mn(II) into Calcite: a Mn K-edge EXAFS Study

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Introduction: Structural distortions around impurities and relaxation phenomena are essential for understanding metal partitioning behavior, stability and physicochemical properties of solid solutions. In this study, the local structure around Mn(II) into a series of $\text{MnCO}_3\text{-CaCO}_3$ solid solutions was determined using EXAFS spectroscopy, particularly focusing on assessing the variation of the first shell Mn-O bond distance among different Mn composition samples.

Methods and Materials: $\text{MnCO}_3\text{-CaCO}_3$ solid solution samples were synthesized at room temperature and/or 60 °C using the method described by Böttcher [1]. Briefly, 2.5 M $(\text{Mn,Ca})\text{Cl}_2$ and 0.025 M NaHCO_3 solutions were mixed to create a supersaturated, metastable solution. Pure nitrogen gas was allowed to flow over the solution-air surface in a sealed vessel, forcing slow degassing of dissolved CO_2 and precipitation of a $(\text{Mn,Ca})\text{CO}_3$ phase. Precipitation generally started within 30-60 min, and samples were filtered after 48 hr, washed repeatedly in deionized water, and dried at 60 °C. Data analysis was done with WinXAS2.0 [2], in combination with the FEFF7 code [3], following standard procedures.

Results: The most important finding is that the first shell Mn-O distances are consistently 2.18-2.19 Å over a wide composition range of the solid solutions ($X_{\text{MnCO}_3} = 0.05\text{-}0.86$) (Figure 1). These observations support Pauling model behavior rather than Vegard's law (sometimes called the virtual crystal approximation (VCA)) reflecting averaging. In contrast, radial distance involving multiple bonds shows a progressive change across the solid solution (Figure 1). We also find that Mn(II) is readily incorporated into the calcite structure with minor structural distortion and relaxation. The topology of the calcite structure is based on corner-shared polyhedra without any edge sharing, which readily allows for distortion required to accommodate impurities in the structure. This structural flexibility allows calcite to accommodate a wide variety of trace or toxic metals in subsurface environments.

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References:

[1] Böttcher (1998) *Marine Chem* **62**: 287-297.

[2] Ressler T. (1997) *J. Physique IV*, **7**, C2-269.

[3] Zabinsky S.I., Rehr J.J., Ankudinov A., Albers R.C., and Eller M.J. (1995) *Phys. Rev. B* **52**, 2995-3009.

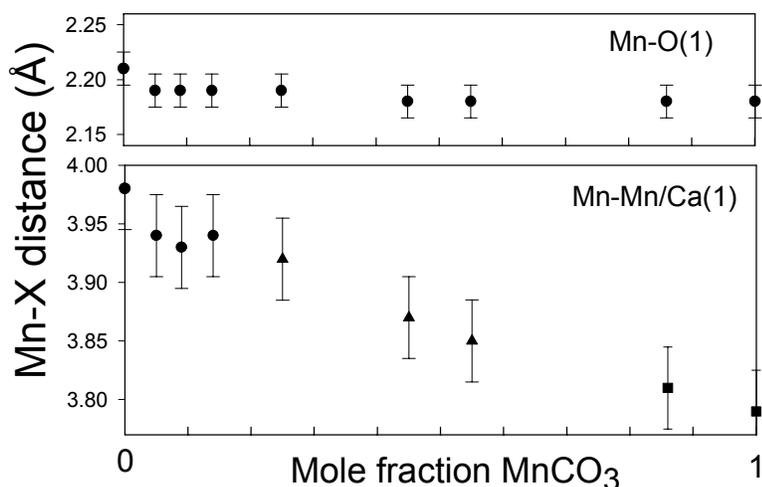


Figure 1. Selected radial distances from Mn determined from EXAFS fitting of the $\text{Mn}_x\text{Ca}_{1-x}\text{CO}_3$ samples.